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Vaporization of Sr- and Mg-Doped Lanthanum Gallate and Implications for Solid Oxide Fuel Cells

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Vaporization of the $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$, and $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ perovskite phases was investigated by the use of Knudsen effusion mass spectrometry in the temperature range of 1618-1886 K. The partial pressures of the gaseous species O_2, Mg, Sr, SrO, Ga, GaO, Ga_2O, and LaO were determined over the samples investigated. The equilibrium partial pressures were used for the calculation of thermodynamic activities of the components at 1800 K. The results are compared with thermodynamic data of $LaGaO_3$(s) without additives. Implications of the present data for the potential use of the material in solid oxide fuel cell technology are discussed as well.
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The $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ perovskite phase with different Sr and Mg content has recently been proposed as a possible candidate material for the electrolyte of solid oxide fuel cells (SOFC).[1] The material shows a good oxygen ion conductivity at about 800°C[2] which is comparable to that of ZrO_2 stabilized with 8 mol % Y_2O_3 (YSZ) at 1000°C. The latter material is commonly used as the solid electrolyte in SOFCs. Electrolytes made of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ are useful for low SOFC operating temperatures. Low operating temperatures between 750 and 800°C allow serious technological and chemical problems to be avoided. The study of the physicochemical properties of this compound is, therefore, of great practical interest. For example, the vaporization processes in the different atmospheres at the anode and cathode sides of the SOFC have to be known under operating conditions. It has been shown that lanthanum gallate vaporizes incongruently,[3,4] which can lead to changes in the chemical composition of the electrolyte and, as a consequence, to a change of its chemical and electrochemical properties. Knowledge of the potential for the decrease of this vaporization by the use of a doped $LaGaO_3$ ceramic electrolyte is, therefore, of practical interest. There are no studies to date dealing with the influence of the partial substitution of alkaline earth metals for La and Ga in $LaGaO_3$ on the volatility of the doped material.

A further problem might be the alkaline earth carbonate formation in $LaGaO_3$ base electrolytes if H_2/CO anode gases are used.[5] Thermodynamic activities of the alkaline earth metal oxides SrO and MgO in $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ have to be known in order to make predictions about carbonate formation.[6]

This paper reports on experimental investigations of the vaporization of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ perovskite phase carried out by Knudsen effusion mass spectrometry. Thermodynamic activities of oxide components in $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ are determined. The results are used to predict the vaporization of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ under SOFC operating conditions at the anode and cathode sides. Implications of the data for the potential use of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ in SOFC technology are discussed.

Experimental

Two samples of the composition $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$ were prepared by different methods: standard solid-state reaction (sample A) and Pechini method[7] (sample B). In the standard solid-state reaction method stoichiometric amounts of powders of La_2O_3 (Fluka AG, 99.99%) and Ga_2O_3 (Chempur, 99.99%), SrO (Schuchardt, Munich, pure anal.), and MgO (Merck, pure anal.) were mixed with acetone and a binder [EtOH + 5% Zusoplast + 2% polyvinylalcohol (PVA)] in an agate mortar for 15 min and calcined at 1273 K for 24 h in air. The calcined powder was ground again in an agate mortar and pressed into pellets. After sintering the pellets at 1773 K for 24 h in air, the sample was characterized by X-ray diffraction (XRD, X'Pert, Philips, Cu Kα). The XRD patterns obtained are presented in Fig. 1. $La(NO_3)_3 \cdot 6H_2O$ (Merck, min 99.0%), Ga (Chempur, 99.999%), $Mg(NO_3)_2 \cdot 6H_2O$ (Chempur, 99.9$^+$%), $Sr(NO_3)_2$ (Riedel-de-Haean, min 99%), citric acid, and ethyl glycol were used as starting materials in the preparation of sample B by the Pechini method.[7] Metallic gallium was solved in HNO_3 (pure anal.) before the preparation of the sample. The sample was calcined at 1273 K for 20 h in air. The calcined powder was ground again in an agate mortar and pressed into pellets. After sintering the pellets at 1673 K for 17 h in air the sample was characterized by XRD (see Fig. 1). Sample B was, in addition, analyzed by the inductively coupled plasma-optical emission spectra (ICP-OES) method to check the deviation from the nominal chemical composition of the prepared sample. Results are given in Table I.

A sample of the composition $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ supplied by ECN, Petten, The Netherlands, was additionally investigated and the results obtained were compared with those obtained for a sample prepared by us. Figure 1 shows the XRD pattern of samples used in this study. The $SrLaGa_3O_7$(s) phase was detected in both samples of the compositions $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$ (A and B) in addition to the main perovskite phase. The $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ sample (C) showed XRD patterns originating from four phases as presented in Fig. 1.

The vaporization studies of the samples were carried out by Knudsen effusion mass spectrometry at Research Center Jülich (see, *e.g.*, Ref. 8, 9). The instrument of the MAT 271 type was supplied by Finnigan MAT, Bremen, Germany, and is completely computer controlled. The vapor species were ionized with an emission current of 1 mA and an electron energy of 50 eV. Knudsen cells made of tungsten and lined completely with iridium were employed in the measurements. Temperatures were measured by an automatic pyrometer of the ETSO-U type supplied by Dr. Georg Maurer GmbH, Kohlberg, Germany, and calibrated using the melting points of nickel, silver, gold, and platinum.

Six runs were carried out in order to elucidate the vaporization of the different samples. The partial pressure of gallium oxide was slightly decreasing at the beginning of each run and became nearly constant after *ca.* 1 h of vaporization at about 1750 K. The runs started at a comparatively high measurement temperature after the ion intensities became time-independent. The measurement of ion intensities was subsequently carried out at different decreasing temperatures. Finally, several increasing temperatures were adjusted af-

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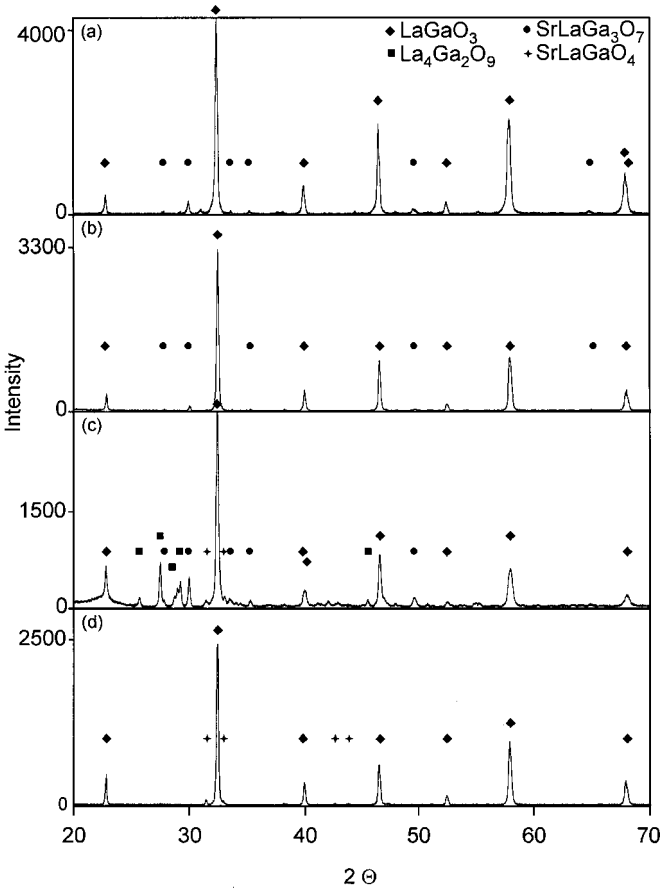

Figure 1. X-ray patterns of the samples A (a), and B (b), both of the composition $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$, and of the sample C (c) ($La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$) after preparation and of sample B (d) after the vaporization measurements.

Table I. Results of chemical analysis (by ICP-OES) of sample B of the composition $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$ after preparation and after the vaporization study by KEMS (runs 4 and 5).

	x (La)	*x* (Sr)	*x* (Ga)	*x* (Mg)
Nominal	0.425	0.0750	0.425	0.075
After preparation	0.428	0.0720	0.428	0.0725
After vaporization study	0.438	0.0735	0.415	0.0740

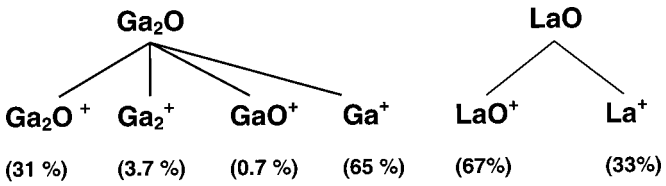

Figure 2. Fragmentation patterns of the Ga_2O(g) and LaO(g) molecules on electron impact ionization.

ter reaching the lowest temperature of the measurement range in order to show the reproducibility of the vapor pressure measurements. Runs 1-3 (sample A) and 4 and 5 (sample B) were carried out for the same material. Between the runs, the samples were taken out of the effusion cell, ground in an agate mortar to refresh the vaporization surface, and studied again. The residual of sample B after run 5 was analyzed by means of chemical analysis (Table I) and XRD (Fig. 1) to check the possible change of sample due to depletion of Ga_2O_3 from the sample during the vaporization measurement. The relative accuracy of the chemical analysis performed by ICP-OES method (instrument 34000-459 B, Fisons/ARL, Switzerland) was ±3%.

Results

Ionic species and their assignment to neutral precursors.—The ion species O_2^+, Ga^+, Ga_2^+, GaO^+, Ga_2O^+, Mg^+, Sr^+, SrO^+, La^+, and LaO^+ were detected in the mass spectrum of the vapor over the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples. They were identified by their mass, by the shutter effect, and by their isotope abundances. The O^+ signal originating from the samples was not detected because of interfering background ion intensities at $m/e = 16$ amu. The assignment of the Ga-containing ions to their neutral precursors was carried out by the use of isothermal vaporization experiments of La_2O_3-Ga_2O_3 samples and was reported in Ref. 4. It was assumed that the other ion species are formed from the gaseous neutral species determined by Chupka *et al.*[10] on vaporizing pure La_2O_3 and by Porter *et al.*[11] on vaporizing pure MgO and SrO. The assignment of the ions to their neutral precursors is given in Table II. Fragmentation patterns of the Ga_2O and LaO molecules, as determined in Ref. 4 are presented in Fig. 2.

Figure 3 exemplifies the ion intensities corrected for isotopic distribution, as measured in run 6 at different temperatures on vaporizing the sample $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$. The ion intensities obtained from runs 1-6 at 1800 K by interpolation are listed in Table II.

Partial pressures.—Partial pressures $p(\mathrm{i})$ of the species i at the temperature T were obtained from the equation

Table II. Chemical composition, temperature range of vaporization measurement, and mass spectra corrected for isotopic distributions for the LSGM samples at 1800 K.

Sample	Run	Chemical composition	ΔT (K)	O_2	Ga(g)	Ga_2O(g)		GaO(g)	LaO(g)		Mg(g)	Sr(g)	SrO(g)
		$LSGM_{x-y}$[a]		O_2^+	Ga^+	Ga_2O^+	Ga_2^+	GaO^+	La^+	LaO^+	Mg^+	Sr^+	SrO^+
A	1	LSGM 15-15	1629-1837	2190	47400	7840	1110	182	—	—	195	53.3	11.4
A	2	LSGM 15-15	1639-1860	1830	42800	6480	979	174	—	—	246	42.2	13.6
A	3	LSGM 15-15	1618-1831	1670	39600	5950	851	148	—	—	—	58.0	13.3
B	4	LSGM 15-15	1652-1844	4280	53070	9290	1480	351	1.3	3.6	247	21.7	5.4
B	5	LSGM 15-15	1669-1850	4250	50500	9020	1420	359	2.2	3.6	263	24.0	4.2
C	6	LSGM 10-20	1631-1886	2330	35800	6940	1040	223	0.85	2.7	262	24.4	4.5

[a] x and y are mole fractions, in percent, of Sr and Mg, respectively, in the La and Ga sublattices of the $LaGaO_3$ perovskite.

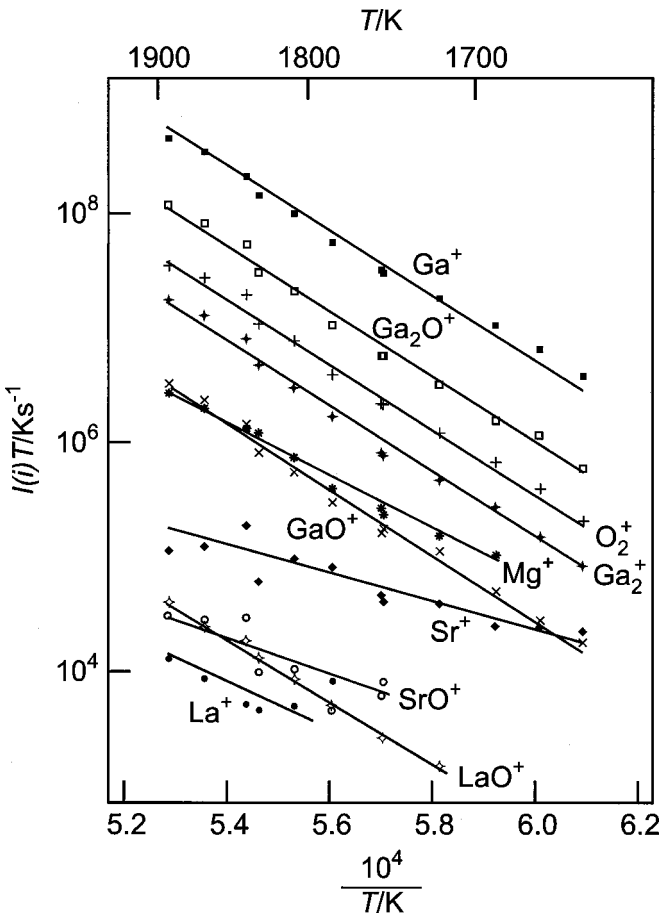

Figure 3. Ion intensities obtained in run 6 for different temperatures.

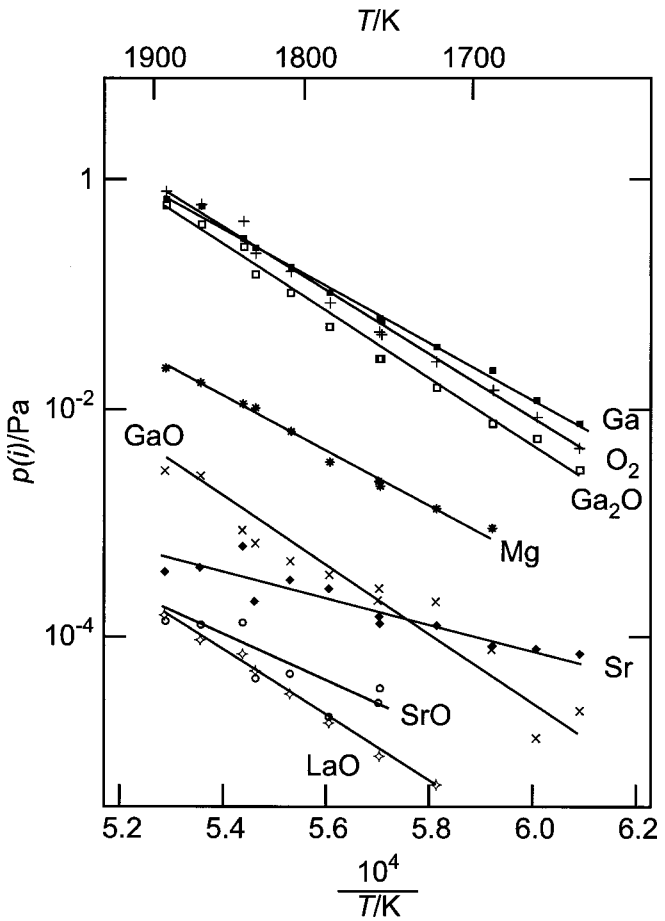

Figure 4. Vapor pressures over the sample LSGM 10-20 obtained in run 6.

$$p(\mathrm{i}) = \{kT\Sigma I(\mathrm{i})\}/\sigma(\mathrm{i}) \quad [1]$$

where k and $\Sigma I(\mathrm{i})$ are the pressure calibration factor and the sum of the intensities of the ions originating from the same neutral precursor i. $\sigma(\mathrm{i})$ is the relative ionization cross section of the species i. The values of the relative ionization cross sections $\sigma(\mathrm{i})$ given in parentheses were used for the following gaseous species i: Ag (5.35), Au (6.82), Ni (5.08), O_2 (1.25), Ga (8.62), GaO (6.12), Ga_2O (18.1), LaO (10.7), Mg (3.39), Sr (8.88), and SrO (6.30). They were obtained on the basis of the cross sections of the elements given in Ref. 12-15 and from the empirical ratios $\sigma(\mathrm{MO})/\sigma(\mathrm{M}) = 0.71$ and $\sigma(\mathrm{MO_2})/\sigma(\mathrm{MO}) = 0.36$ selected from the data reported by Drowart[16] for the transition metals M.

Pressure calibration was carried out by vaporizing pure Ag, Au, and Ni at their melting temperatures. The pressure calibration constant k amounted to $(4.85 \pm 0.57)10^{-8}$ Pa s K^{-1} (runs 1-3), $(2.72 \pm 0.33)10^{-8}$ Pa s K^{-1} (runs 4 and 5), and $(2.82 \pm 0.34)10^{-8}$ Pa s K^{-1} (run 6) for the runs given in parentheses. Partial pressures were evaluated by the use of Eq. 1 for each measurement temperature. In Fig. 4 we show as an example the partial pressures of vapor species obtained in run 6 for the sample $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$. Table III shows the partial pressure equations of the different species obtained for all measurements.

Thermodynamic activities.—The determination of the thermodynamic activities of Ga_2O_3, MgO, and SrO in the samples was carried out by vaporizing pure Ga_2O_3, MgO, and SrO before and after the measurement of a sample. The equilibria

$$\underline{Ga_2O_3} = Ga_2O(g) + O_2(g) \quad [2]$$

$$\underline{MgO} = Mg(g) + \tfrac{1}{2}O_2(g) \quad [3]$$

$$\underline{SrO} = SrO(g) \quad [4]$$

were evaluated from the measurements of the sample materials and the pure components. Ga_2O_3, MgO, and SrO mean the respective oxide components in the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples or these oxides as pure materials. The following equations result for the computation of the thermodynamic activities by considering the equilibrium constants $K_p^o(2)$, $K_p^o(3)$, and $K_p^o(4)$ of the reactions Eq. 2 to 4

$$a(Ga_2O_3) = \frac{I(Ga_2O^+) \cdot I(O_2^+)}{I^o(Ga_2O^+) \cdot I^o(O_2^+)} \quad [5]$$

$$a(\mathrm{MgO}) = \frac{I(Mg^+) \cdot I(O_2^+)^{1/2}}{I^o(Mg^+) \cdot I^o(O_2^+)^{1/2}} \quad [6]$$

and

$$a(\mathrm{SrO}) = \frac{I(SrO^+)}{I^o(SrO^+)} \quad [7]$$

$I^o(\mathrm{i})$ denotes the ion intensities detected on vaporizing the pure oxides. Thermodynamic activities resulted for each of the measurement temperatures of the runs 1 to 6 by using Eq. 5-7 and the measured ion intensities for the samples and for the pure components. The intensities for pure Ga_2O_3(s) (1479-1753 K), MgO(s) (1636-2029 K), and SrO(s) (1651-2272 K) were measured in the temperature ranges given in parentheses.

Table III. Partial pressure equations, $\ln p(i) = -A/T + B$, for the vapor species over LSGM samples.[a]

		O_2(g)		Ga(g)		GaO(g)		Ga_2O(g)		Mg(g)		Sr(g)		SrO(g)	
Run	Sample	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	A	59898	30.837	56040	29.361	55172	22.137	68361	35.270	83039	40.264	34096	10.778	37811	11.705
2	A	66085	34.115	58882	30.945	57586	23.632	68251	35.084	79194	38.167	44795	16.555	35002	10.326
3	A	47995	23.974	59104	31.000	66096	28.591	63839	32.548	-	-	47890	18.470	50864	19.120
4	B	51907	27.057	52663	27.598	52791	22.568	62911	32.438	58307	26.758	28843	6.994	48248	16.716
5	B	56782	29.752	51383	26.823	52478	22.488	62086	31.949	55631	25.334	24260	4.548	46310	15.394
6	C	62490	32.396	59109	30.754	53860	22.424	66317	34.080	63316	29.634	30792	8.227	38762	11.312

[a] LaO(g) was identified only at the highest measurement temperatures in runs 4-6.

The activity of La_2O_3 could only be estimated due to the very small intensities of the ions La^+ and LaO^+ observed on vaporizing the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples. The estimation was carried out for runs 4 and 5 considering the equilibrium

$$\underline{La_2O_3}(s) = 2LaO(g) + 1/2O_2(g) \quad [8]$$

in the sample material and in the sample of the composition {42 mol % Ga_2O_3 + 58 mol % La_2O_3}. The latter sample consists of the two phases $LaGaO_3$(s) and $La_4Ga_2O_9$(s); the activity of La_2O_3 in this sample at 1800 K was previously determined by us as 0.47.[4] The thermodynamic activity in the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ sample was evaluated from the equation

$$a(La_2O_3) = \frac{\{I(LaO^+)^2 I(O_2^+)^{1/2}\}_{LSGM}}{\{I(LaO^+)^2 I(O_2^+)^{1/2}\}_{LG}} 0.47 \quad [9]$$

where LSGM and LG means that the ion intensities were measured over the sample $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$ (sample B) and over the two-phase sample {$LaGaO_3$+$La_4Ga_2O_9$}, respectively.

Table IV summarizes the thermodynamic activities of the components in the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples at 1800 K obtained by all runs.

Discussion

Implications for SOFC.—Vaporization of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ is an important property for the technical application of this material and for its production process (*e.g.*, sintering). It is shown that this material vaporizes incongruently mainly in the form of the different Ga-containing species and oxygen. The volatility of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ materials depends on the oxygen partial pressure of the surrounding atmosphere and the temperature. The volatility of the material under SOFC operating conditions is important for its practical use as an electrolyte in SOFCs. The composition $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ is most important for practical application due its high ionic conductivity. The estimation of the volatility was, therefore, carried out for this composition. In addition, different H_2/H_2O ratios were selected covering the range present at the anode side and a temperature of 1073 K. Figure 5 shows the results of the computations carried out by using the thermodynamic activity of Ga_2O_3 at 1073 K and the F*A*C*T 2.2 program[17] together with the thermodynamic data of the different gaseous species given in the F*A*C*T 2.2 database. The thermodynamic activity of Ga_2O_3 in $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ was estimated from the value at 1800 K in Table IV by assuming that the chemical potential of Ga_2O_3 in $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ is independent of temperature. This assumption is based on the general experience that the Gibbs energy of formation of the perovskites from their component oxides is practically temperature independent. A value of $a(G_2O_3) = 2.3 \cdot 10^{-5}$ thus resulted for 1073 K.

Figure 5 shows that the volatility of Ga_2O_3 in $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ at the anode side of SOFC is high. The high volatility is due to the formation of GaOH(g) and decreases if the H_2O/H_2 ratio is raised. The latter means that the volatility is the highest at the entrance of the fuel gas. The partial pressure of the most abundant vapor species GaOH at the anode side changes by less than a factor of 1.8 if the temperature is reduced from 1073 to 973 K. That means a decrease of the operating SOFC temperature by 100 K reduces the Ga_2O_3 vaporization only slightly. The results indicate that the use of electrolytes made of $LaGaO_3$ base perovskites without protective measures at the anode side of SOFC can be a problem.

The values for the thermodynamic activity of MgO and SrO in $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ are high (cf. Table IV) and can be

Table IV. Thermodynamic activities of the LSGM components obtained at 1800 K.

Run	Sample	$a(Ga_2O_3) \times 10^3$	a(MgO)	a(SrO)	$a(La_2O_3)$[a]
1	A	2.9	0.50	0.76	
2	A	2.0	0.59	0.90	
3	A	1.6	—	0.89	
4	B	2.9	0.61	0.36	0.3
5	B	2.4	0.64	0.28	0.3
6	C	1.7	0.70	0.30	

[a] Estimated values.

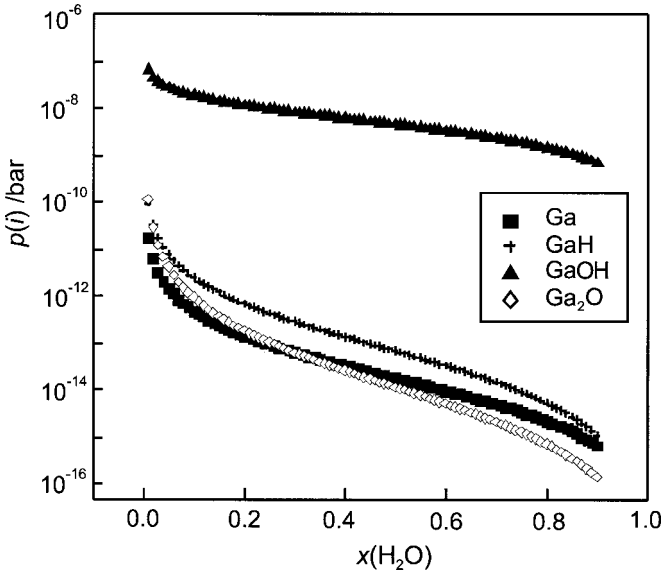

Figure 5. Partial pressures over the sample of the composition $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ in an H_2/H_2O atmosphere at 1073 K for different H_2O mole fractions.

used to estimate the conditions for the formation of $MgCO_3$ and $SrCO_3$ under an atmosphere present at the anode according to the reactions

$$\underline{MgO} + CO_2(g) = MgCO_3(s) \quad [10]$$

$$\underline{SrO} + CO_2(g) = SrCO_3(s) \quad [11]$$

where $\underline{MgO}$ and $\underline{SrO}$ means MgO and SrO bound in the perovskite. By using $a(MgO) = 0.40$, $a(SrO) = 0.13$, a CO_2 partial pressure of 0.1 bar, and the data from the IVTANTHERMO database[18] the following relations are obtained for the change of the Gibbs energy of reactions Eq. 10 and 11

$$\Delta_f G(T)/J\,mol^{-1} = -99743 + 199.63T \text{ for } MgCO_3 \quad [12]$$

and

$$\Delta_f G(T)/J\,mol^{-1} = -229890 + 193.29T \text{ for } SrCO_3 \quad [13]$$

This means that the formation of $MgCO_3$ and $SrCO_3$ is possible at temperatures below 500 and 1189 K, respectively; the compounds are not stable at temperatures above this value. The temperature dependence of the thermodynamic activity of MgO and SrO is small for high activity values, which is the case if the chemical potential is assumed to be temperature independent.

Condensed phase equilibria.—Samples A and B of the chemical composition $La_{0.85}Sr_{0.15}Ga_{0.85}Mg_{0.15}O_{2.85}$ contained the $SrLaGa_3O_7$ phase in addition to the perovskite phase after preparation. This was independent from the preparation method as can be seen in Fig. 1. According to the phase diagram studies carried out by us, the sample should, however, be a single phase.[19] A possible reason for this observation might be a small overstoichiometry in the Ga_2O_3 component. This was, however, not confirmed by the chemical analysis of sample B conducted with a fresh-prepared sample (see Table I).

XRD analysis of the sample B residual from the Knudsen cell shows the rearrangement of solid phases during the vaporization measurement. The $SrLaGa_3O_7$ phase disappeared and the $SrLaGaO_4$ phase was identified in this residual besides the perovskite phase. According to phase diagram of the system (Ref. 19), the $SrLaGaO_4$ phase becomes stable in this case.

Sample C of the chemical composition $La_{0.90}Sr_{0.10}Ga_{0.80}Mg_{0.20}O_{2.85}$ contained the four phases $LaGaO_3$, $La_4Ga_2O_9$, $SrLaGa_3O_7$, and $SrLaGaO_4$ before the vaporization study (see Fig. 1). This might be caused by the incomplete reaction of the starting components during the sample preparation. Phase relations in the quasi-quaternary Ga_2O_3-La_2O_3-MgO-SrO system show that these phases cannot exist together in thermodynamic equilibrium. Equilibration is assumed at the beginning of the vaporization experiments.

The partial pressures of the gallium-containing species were slightly decreasing at the beginning of the vaporization experiments. This might be explained by the continuous Ga depletion from the samples resulting in the formation of additional phases in the samples. Therefore, thermodynamic data obtained in this study always refer to the B site poor perovskite phase. This phase remains in equilibrium with other phases depending on the quasi-quaternary phase diagram, which is still little known. However, as follows from chemical analysis of the initial sample and of the residuals after the vaporization study carried out for sample B, the total composition of samples changes only slightly during the experiment. This means, that the amount of other phases formed in the Knudsen cell is often too small to identify all of them by means of XRD analysis.

Consistency and uncertainties of data.—The thermodynamic activities of Ga_2O_3 in the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples are similar to the value for undoped $LaGaO_3$, $2.17 \cdot 10^{-3}$ at 1700 K and $3.35 \cdot 10^{-3}$ at 1800 K.[4] It is interesting to note that the thermodynamic activities of the oxide components in the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ samples do not depend on the oxygen partial pressure since the oxygen vacancies, δ, in the perovskite structure are independent from the oxygen partial pressure. This is in contrast to other doped perovskites containing transition metals (*e.g.*, Ref. 20).

The thermodynamic activity of Ga_2O_3 could be also evaluated by use of the equilibrium

$$\underline{Ga_2O_3}(s) = 2Ga(g) + 3/2\ O_2(g) \quad [14]$$

from the equation

$$a(Ga_2O_3) = \frac{\{I(Ga^+ \text{ from } Ga)^2 I(O_2^+)^{3/2}\}}{\{I(Ga^+ \text{ from } Ga)^2 I(O_2^+)^{3/2}\}^o} \quad [15]$$

Values of $1.9 \cdot 10^{-3}$ and $1.7 \cdot 10^{-3}$ were, for example, obtained in this way for the runs 3 and 4, respectively. Taking into account that (*i*) Reaction 14, involves 3.5 gaseous species in comparison to only two species in Eq. 2 and (*ii*) there is the necessity of subtraction of part of the total Ga^+ intensity formed by fragmentation from $Ga_2O(g)$, the use of Eq. 15 in the calculations must be considered as substantially less accurate than the method used in this work. From this point of view, $a(Ga_2O_3)$ values obtained by both methods are in agreement.

We also tried to estimate the SrO activity by use of the equilibrium

$$\underline{SrO}(s) = Sr(g) + 1/2O_2(g) \quad [16]$$

from the equation

$$a(SrO) = \frac{\{I(Sr^+)I(O_2^+)^{1/2}\}_{LSGM}}{\{I(Sr^+)^o I(O_2^+)^{o\,1/2}\}} \quad [17]$$

The values obtained in this way were by 25-100% different from those evaluated by using of Eq. 7. Values of >1 (run 3), 0.21 (run 5), and 0.79 (run 6) resulted, for example, for samples A, B, and C, respectively. Possible reasons of these differences are (*i*) relative large scatter of Sr^+ ion intensities and (*ii*) possible fragmentation of SrO(g) forming Sr^+.

The thermodynamic activities of Ga_2O_3 and MgO in the samples A and B, which are of the same chemical composition, show very good agreement. This is not the case for the SrO activities, which differ by a factor of two to three between both samples as follows from Table IV. Due to the low SrO^+ ion intensity, the activity of SrO was obtained with less accuracy in comparison to the activities of MgO and Ga_2O_3. However, the difference of SrO activity as measured for samples A and B cannot be explained by this uncertainty. The possible reason for this inconsistency might be small differences of sample composition caused by different preparation methods (see Experimental section).

Probable overall uncertainties were not evaluated for the partial pressures given in Table III since it is difficult to estimate uncertainties for the ionization cross sections of gaseous oxide species. In contrast to the partial pressures, the thermodynamic activities do not depend on ionization cross sections but only on ion intensity ratios. This leads to comparatively small uncertainties for the thermodynamic activities. These uncertainties were estimated as 25, 25, and 35%, respectively, for the activities of Ga_2O_3, MgO, and SrO, considering the error of the calibration constant, the statistical scatter, and the error in the extrapolation of the SrO^+ ion intensities up to 1800 K carried out for the calibration measurements using pure SrO. The absolute error of the temperature measurement estimated as ± 10 K was additionally used in the error computation for the thermodynamic activities. The estimated uncertainty of the values of the La_2O_3 activity in sample B is a factor of two.

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